REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
07-06-2017	Final Report	1-Jul-2013 - 31-Mar-2017

4. TITLE AND SUBTITLE

Final Report: Insight Into Multifunctional Reactive Adsorbents: Engaging Chemistry, Porosity, Photoactivity and Conductivity into Decontamination Process

5a. CONTRACT NUMBER
W911NF-13-1-0225

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHORS
Teresa J. Bandosz

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
CUNY - City College of New York
160 Convent Avenue

New York, NY 10031 -9101

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
64082-CH.47

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
The composites of a high porosity and of an increased number of terminal hydroxyl groups were prepared. The synthesized materials were exposed to CWA surrogate vapors (CEES or DMCP) at ambient conditions for various periods of time. The amounts adsorbed of either surrogates or their decomposition products were evaluated based on a weight gain. The products of surface reactions in the headspace or adsorbed on the surface were analyzed by MS. As a final step the active phase were deposited in fibers to create smart textile being able to protect and to detect CWA (based on the color change)

15. SUBJECT TERMS
CWA decontamination, multifunctional adsorbents, porosity, surface chemistry, photoactivity, composites

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Teresa Bandosz
UU	UU	UU	UU		19b. TELEPHONE NUMBER 212-650-6017

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

RPPR
as of 12-Oct-2017

Agency Code:

Proposal Number: **Agreement Number:**

Organization:
Address: , ,
Country:
DUNS Number: EIN:
Report Date: Date Received:
for Period Beginning and Ending
Title:
Begin Performance Period: **End Performance Period:**
Report Term: -
Submitted By: Email:
Phone:

Distribution Statement: -

STEM Degrees: **STEM Participants:**

Major Goals:

Accomplishments:

Training Opportunities:

Results Dissemination:

Plans Next Period:

Honors and Awards:

Protocol Activity Status:

Technology Transfer:

INSIGHT INTO MULTIFUNCTIONAL REACTIVE ADSORBENTS

Teresa J. Bandosz

Department of Chemistry
The City College of New York

OBJECTIVE

- ✓ Evaluation of the reactive adsorption capability for CWA surrogates of novel porous composite adsorbents consisting transition metals oxides, alone or in the mixed phase with the modified graphene phase, and with gold or silver nanoparticles
- ✓ Understanding the basic science related to the activity of these materials as adsorbents and decontamination media
- ✓ Materials engineering/deposition of the active phase on fabrics

Materials: Past efforts

- ✓Iron (hydr)oxide: FERRIHYDRITE
- ✓Copper hydroxynitrate
- ✓Zinc hydroxide

Composites

- ✓With graphite oxide (GO)
- ✓With aminated GO (GOU)
- ✓With AgNP

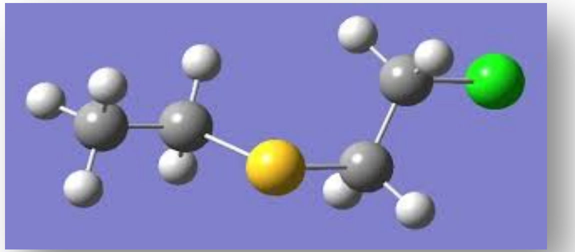
Motivation for the materials' choice

- ☑ Relatively high surface areas
- ☑ Oxygen vacancies as active sites
- ☑ Photoactive in UV-Vis
- ☑ Terminal OH groups
- ☑ GO
  - ☑ enhances dispersion of inorganic phase
  - ☑ provides electronic conductivity for redox reactions
  - ☑ (GOU) activates oxygen
  - ☑ increases surface heterogeneity/defects

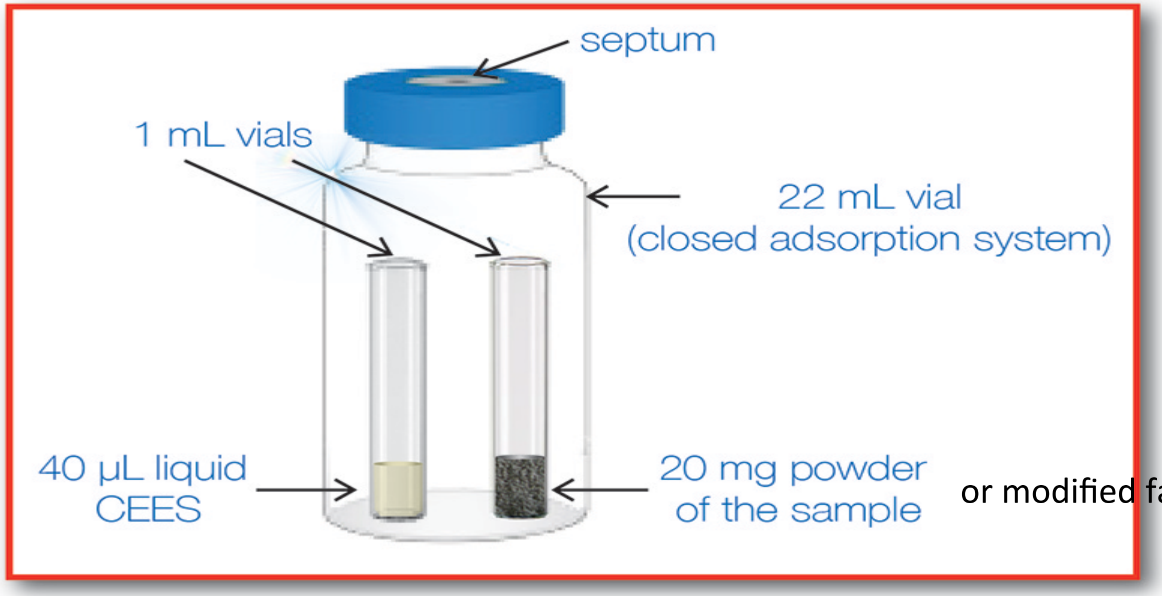
Testing CWA surrogate interactions

Surrogates:

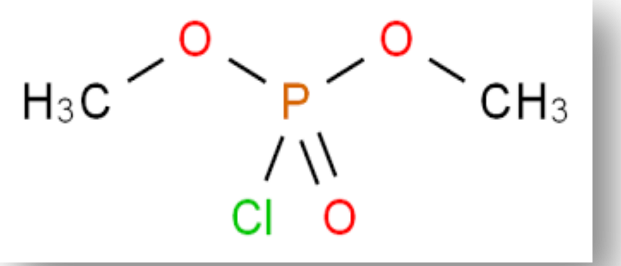
- CEES- 2-chloroethyl ethyl sulfide (HD)



- DMCP- dimethyl chlorophosphate (nerve agents)X)



or modified fabric



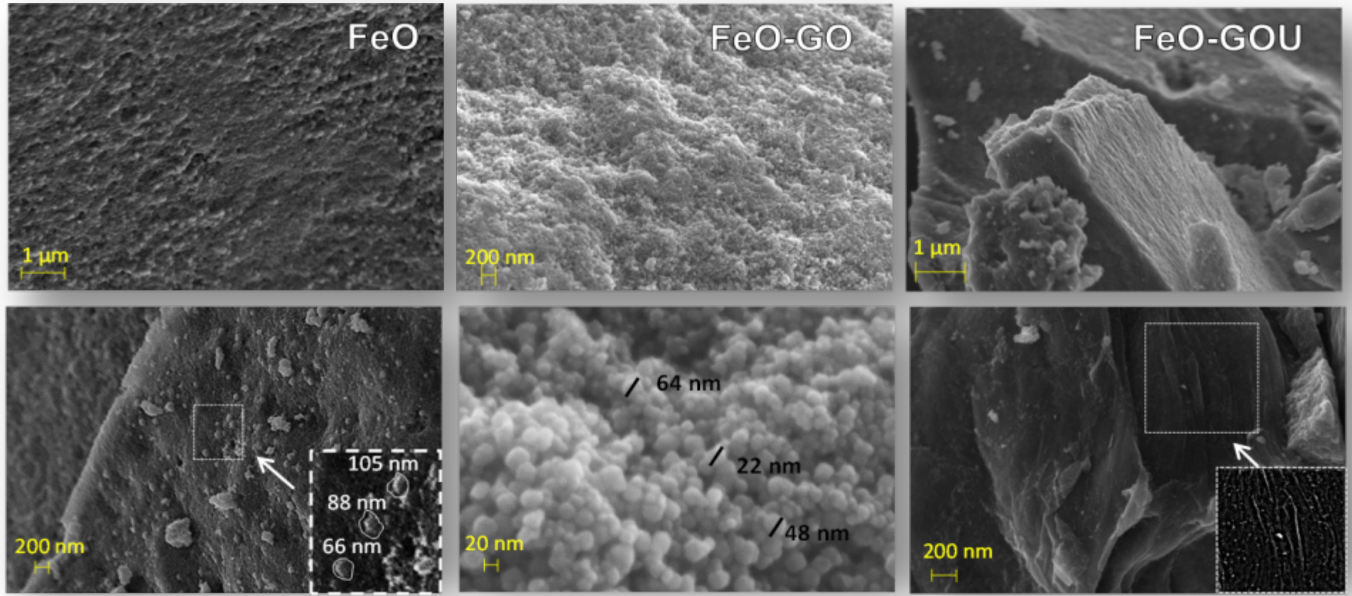
Approaches to derive mechanisms

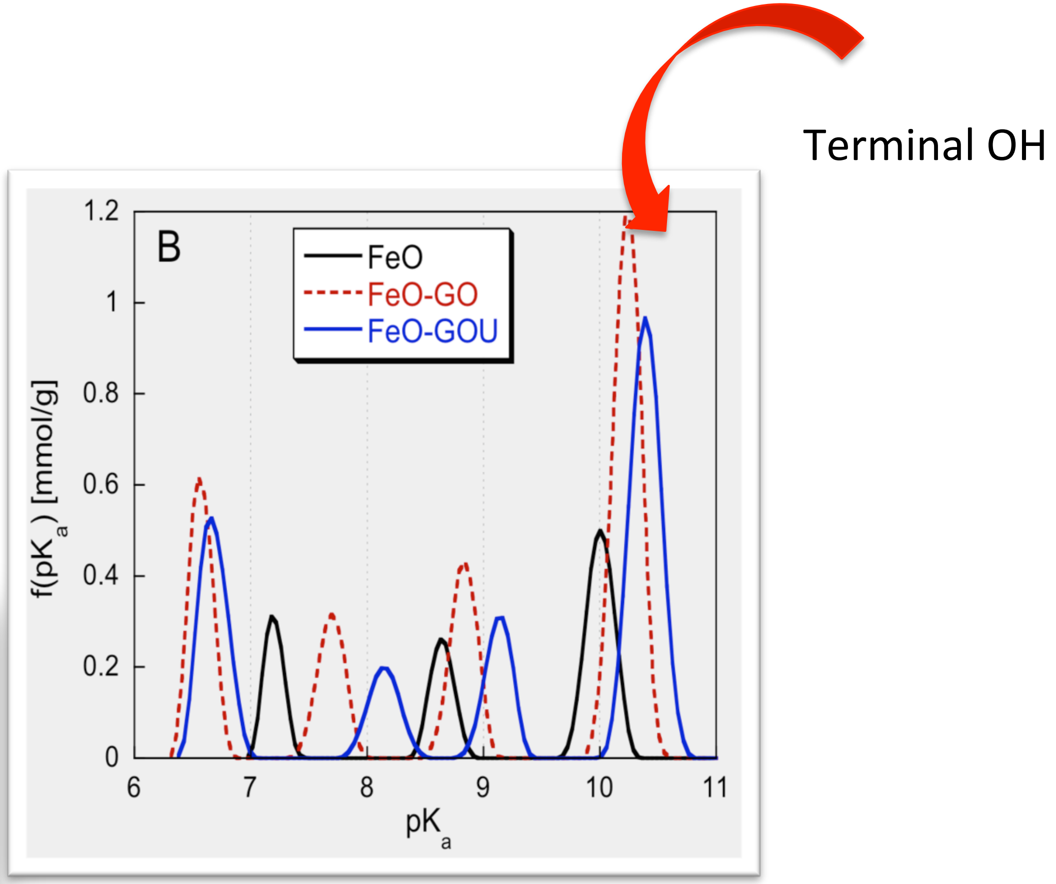
- ✓ Analysis of the surface of initial hydroxides and their composites (porosity, chemistry, microstructure, texture)(N_2, PT, FTIR, SEM, HRTEM..)
- ✓ Analysis of the surface of the exhausted samples (FTIR, TA-MS)
- ✓ Analysis of the surface extraction products (GC

- ✓ -MS)
- ✓ Analysis of the headspace in the close system (GC-MS)

Major Findings: texture and chemistry

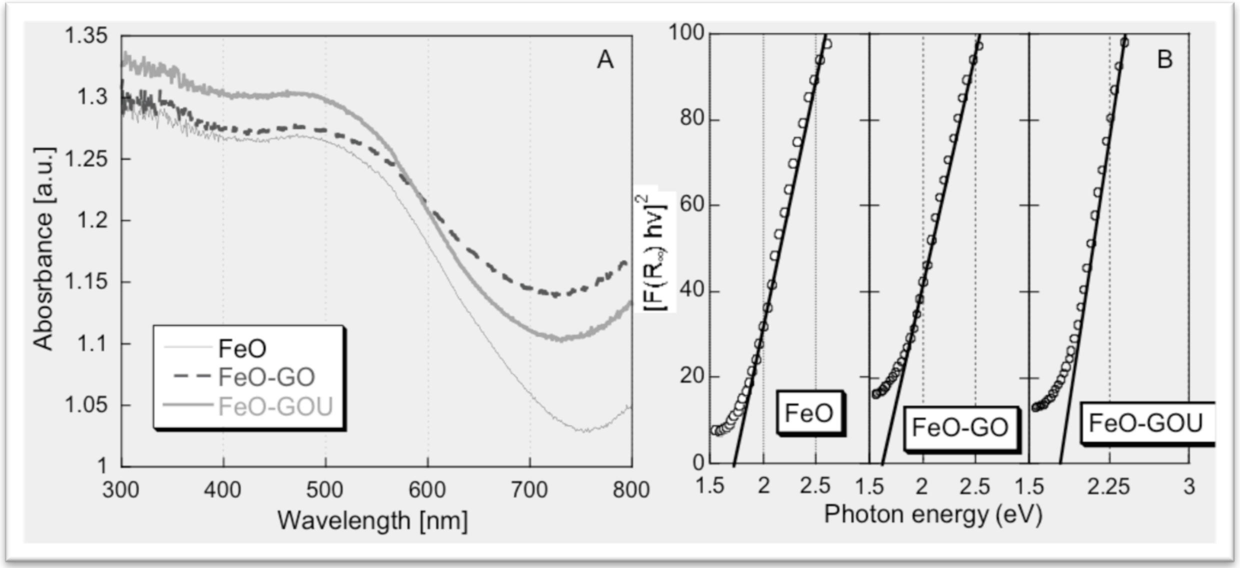
Sample	S^{BET} $[m^2g^{-1}]$	V_T $[cm^3g^{-1}]$	V_{mic} $[cm^3g^{-1}]$	V_{meso} $[cm^3g^{-1}]$	V_{meso}/V_{mic}
FeO	200	0.265	0.073	0.192	2.6
FeO-GO	243	0.304	0.087	0.217	2.5
FeO-GOU	288	0.312	0.102	0.210	2.1

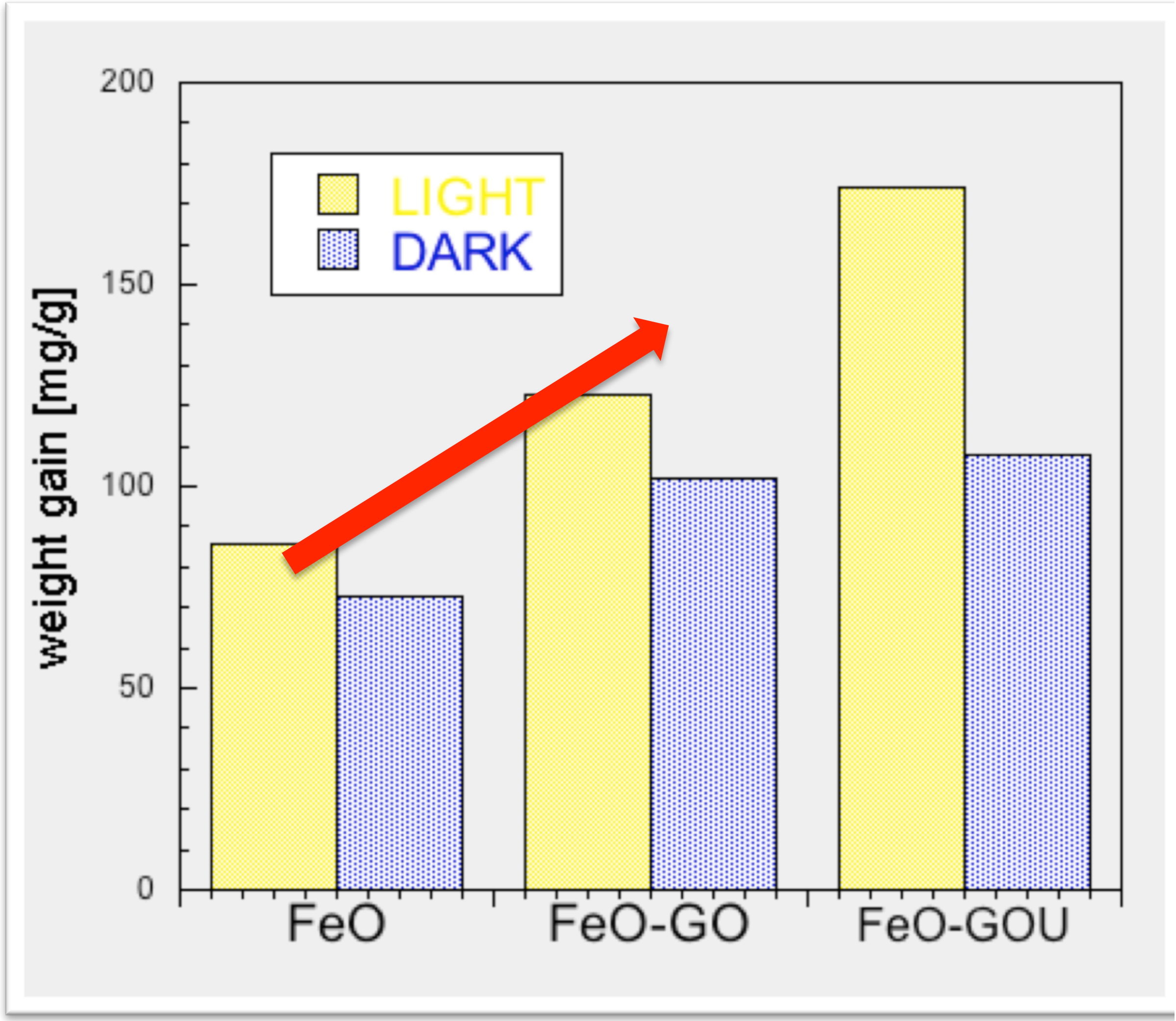




Arcibar Orozco et al. J. Mater.Chem. A 2015, 3, 17080-17090.

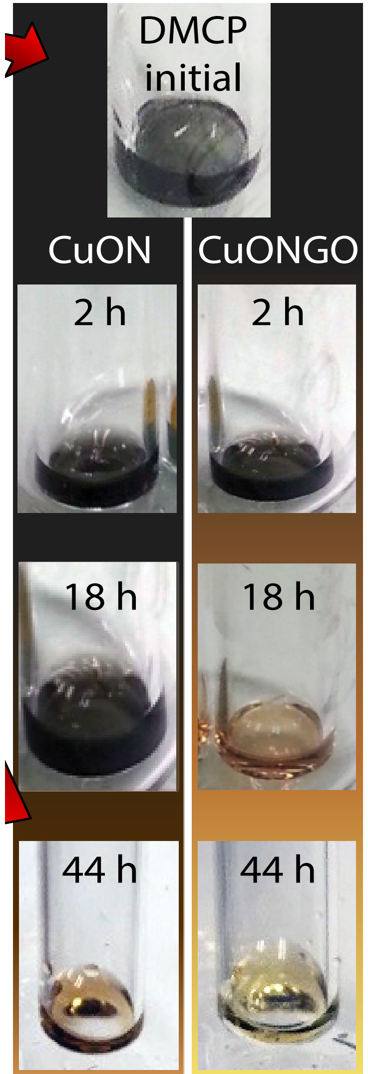
Major Findings: Photoactivity



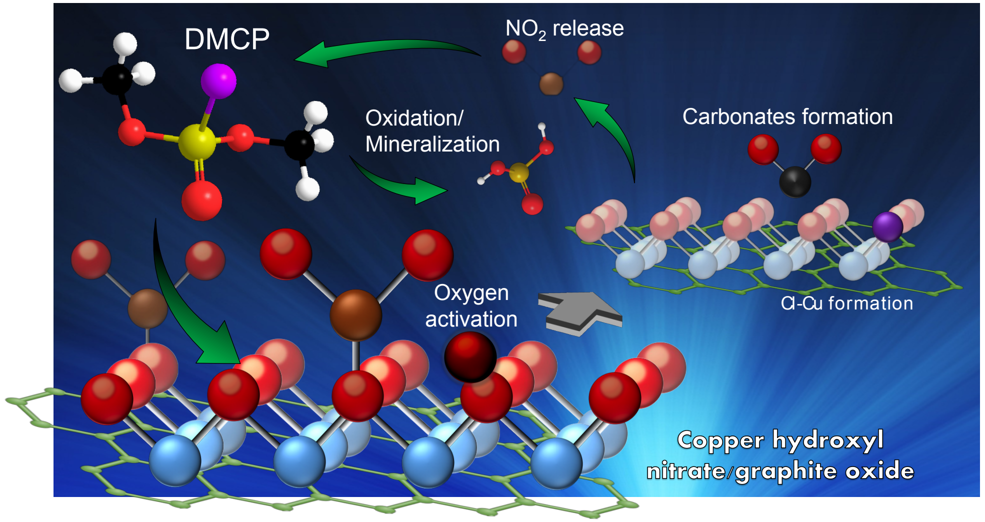


Arcibar-Orozco, et al. J. Mater. Chem. A 3, 2015, 220-231

Major Findings: activity (copper hydroxynitrate)



$H_3PO_4 < H_3PO_4$

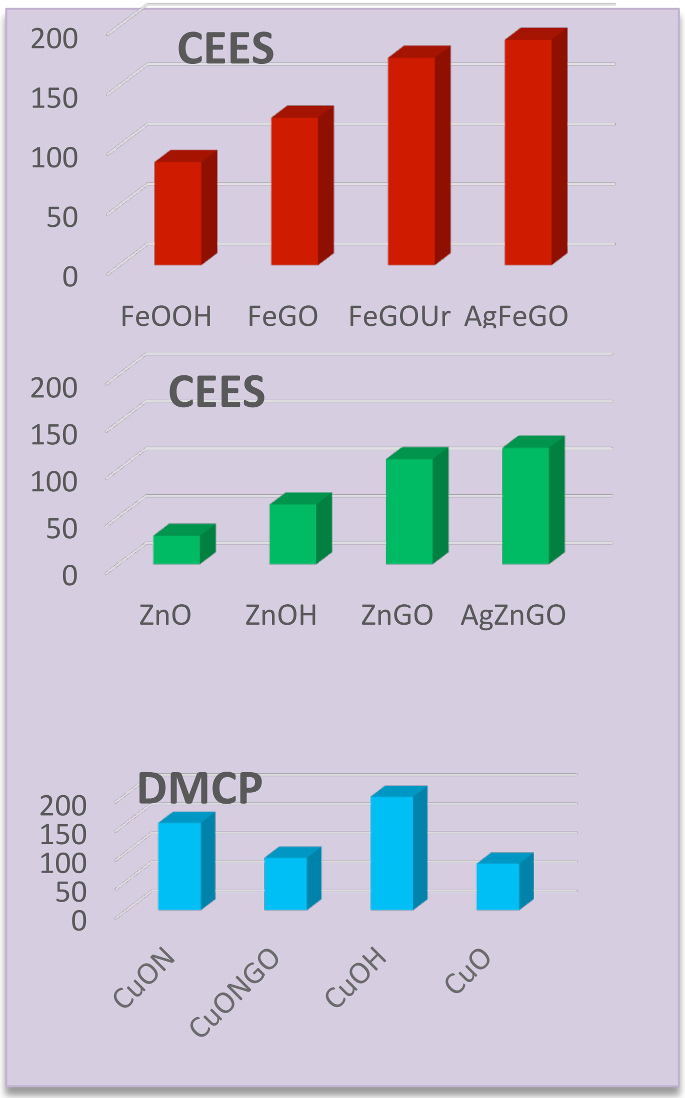


- ✓ H_3PO_4 detection in the liquid
- ✓ NO_2 detection in the headspace

Sample	NO_2 Concentration [ppm]	
	24 h	48 h
CuON	1.3	27.0
CuONGO	15.9	57.6

Arcibar-Orozco, J. Advanced Materials Interfaces, 2015, 2, 1-9

Major Findings: Reactive adsorption



HYDROLYSIS and OXIDATION

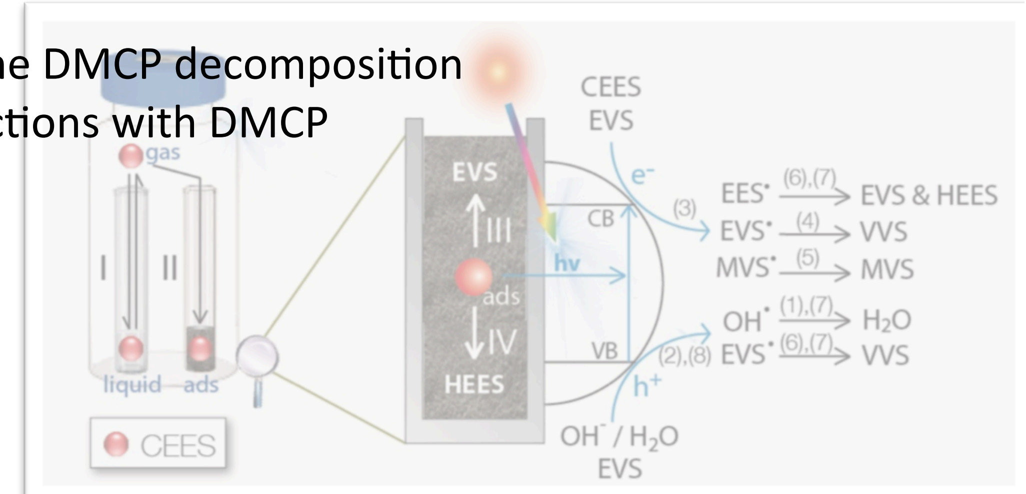
- Both hydrolysis (EVS) and oxidation (CEESO) take place
- GO: increase the oxidation performance
- AgNPs: increase photo-reactivity/radical reaction (disulfides)

HYDROLYSIS and DEGRADATION

- The hydroxyl groups play a key role
- GO: increase the photocatalytic performance
- AgNPs: increased photo-reactivity/radical reaction (disulfides)

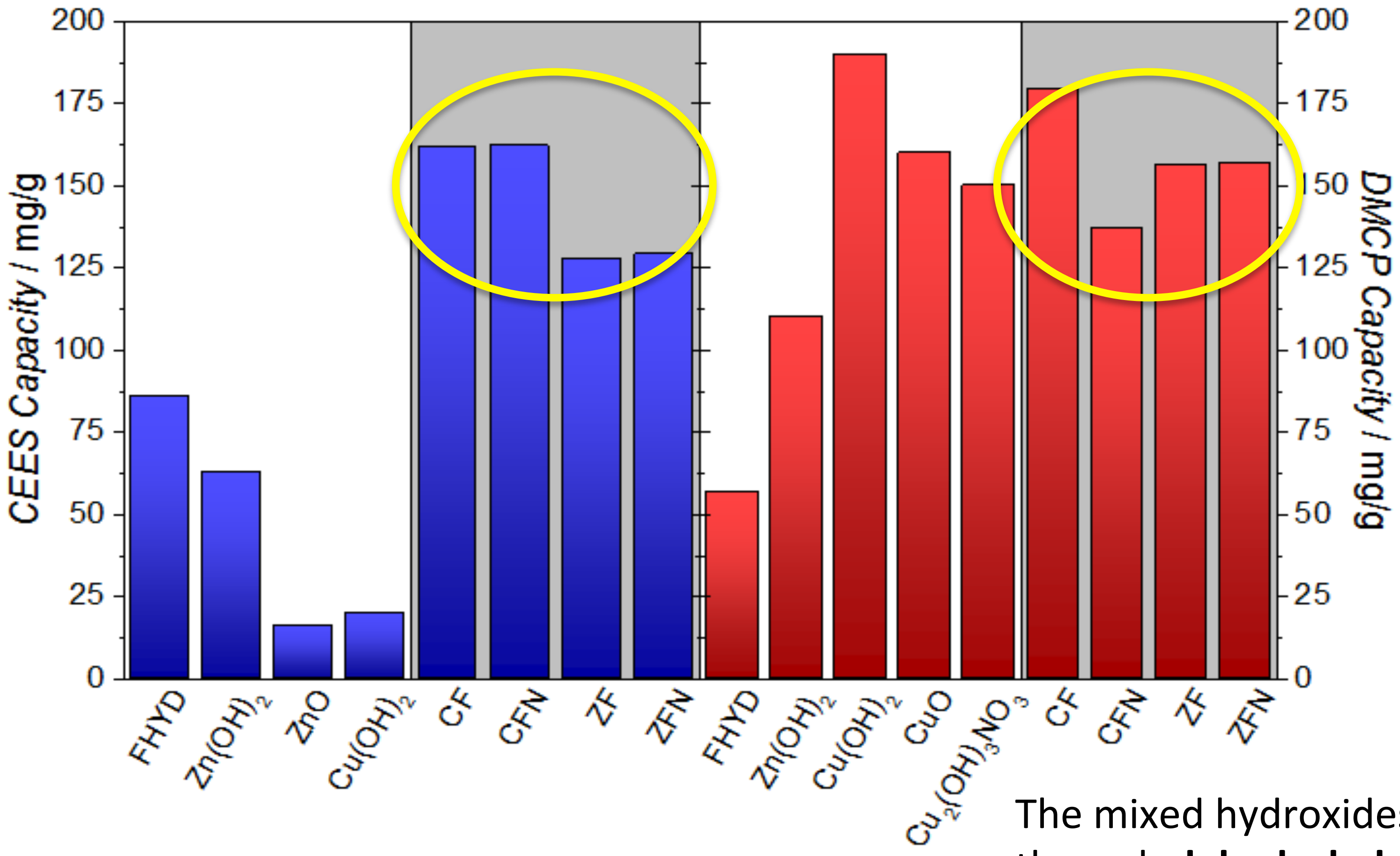
HYDROLYSIS and OXIDATION

- GO considerably accelerates the DMCP decomposition
- Hydroxyl groups: direct interactions with DMCP
- Nitrate groups: NOx formation



Giannakoudakis, D.A. et al. Appl. Catal. B Environ. 2016, 183, 37–46

Major Findings: Mixed oxide performance



C- Cu
F-Fe
Z-Zn
N- Nitrate

The mixed hydroxides are versatile and can detoxify CEES through **dehydrohalogenation** and DMCP through **hydrolysis**.

Florent, M. et al., submitted

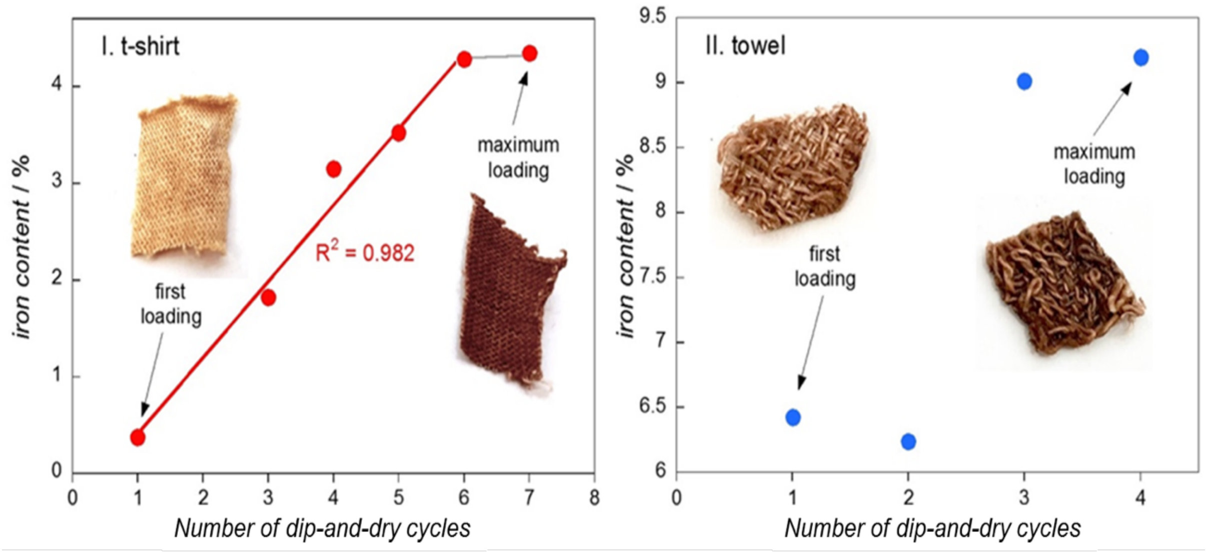
Ferrihydrite on cotton

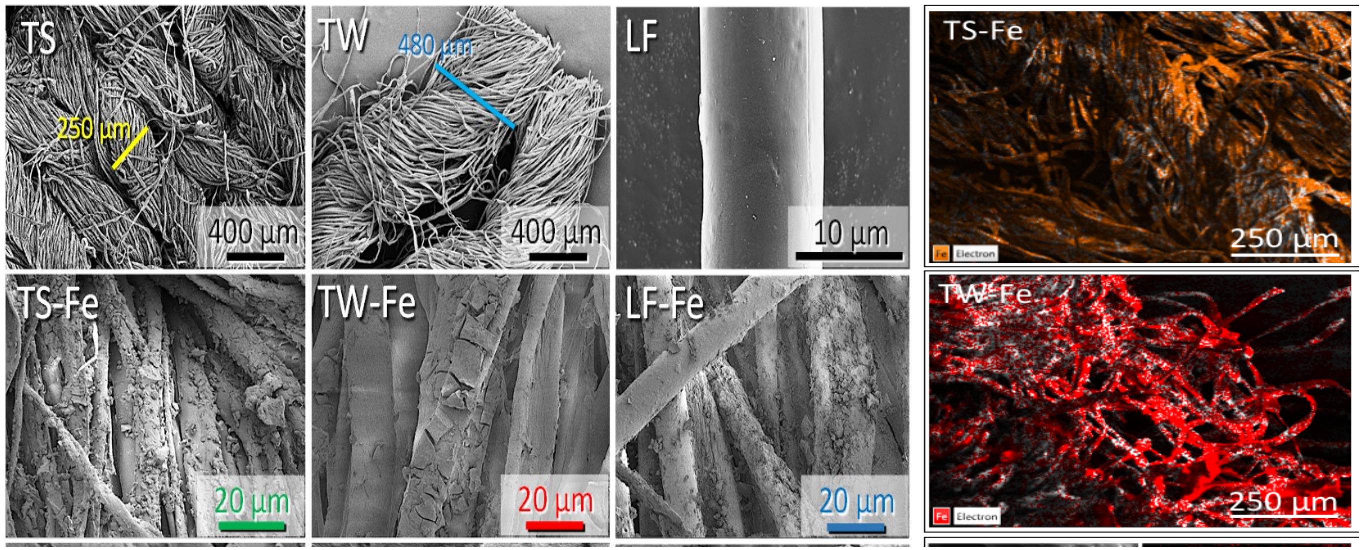
Loose Fibers
7.1% Iron

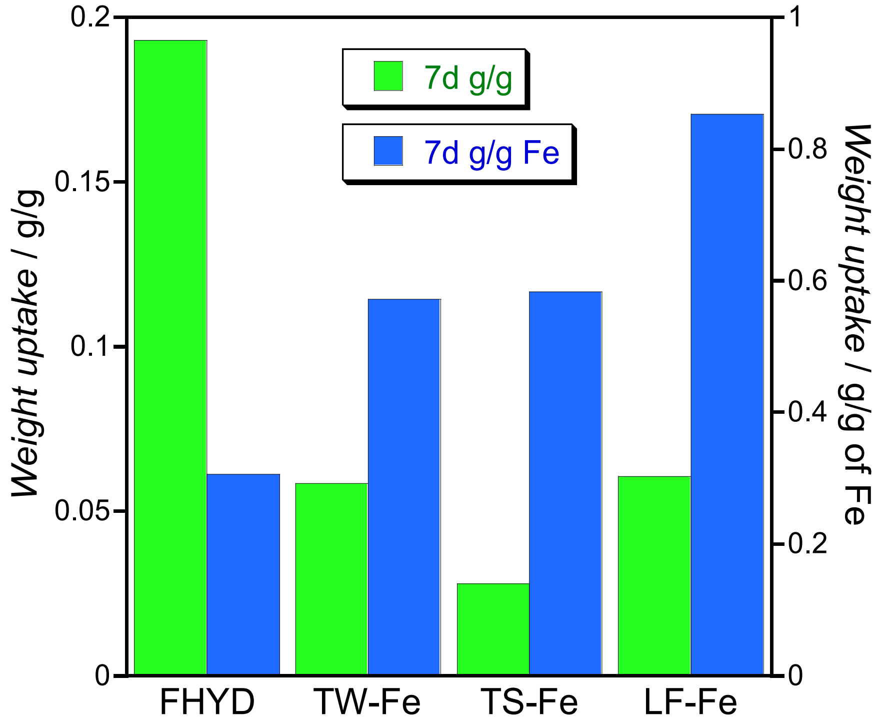
Swatch from TW
10.2% Iron

Swatch from TS
4.8 % Iron

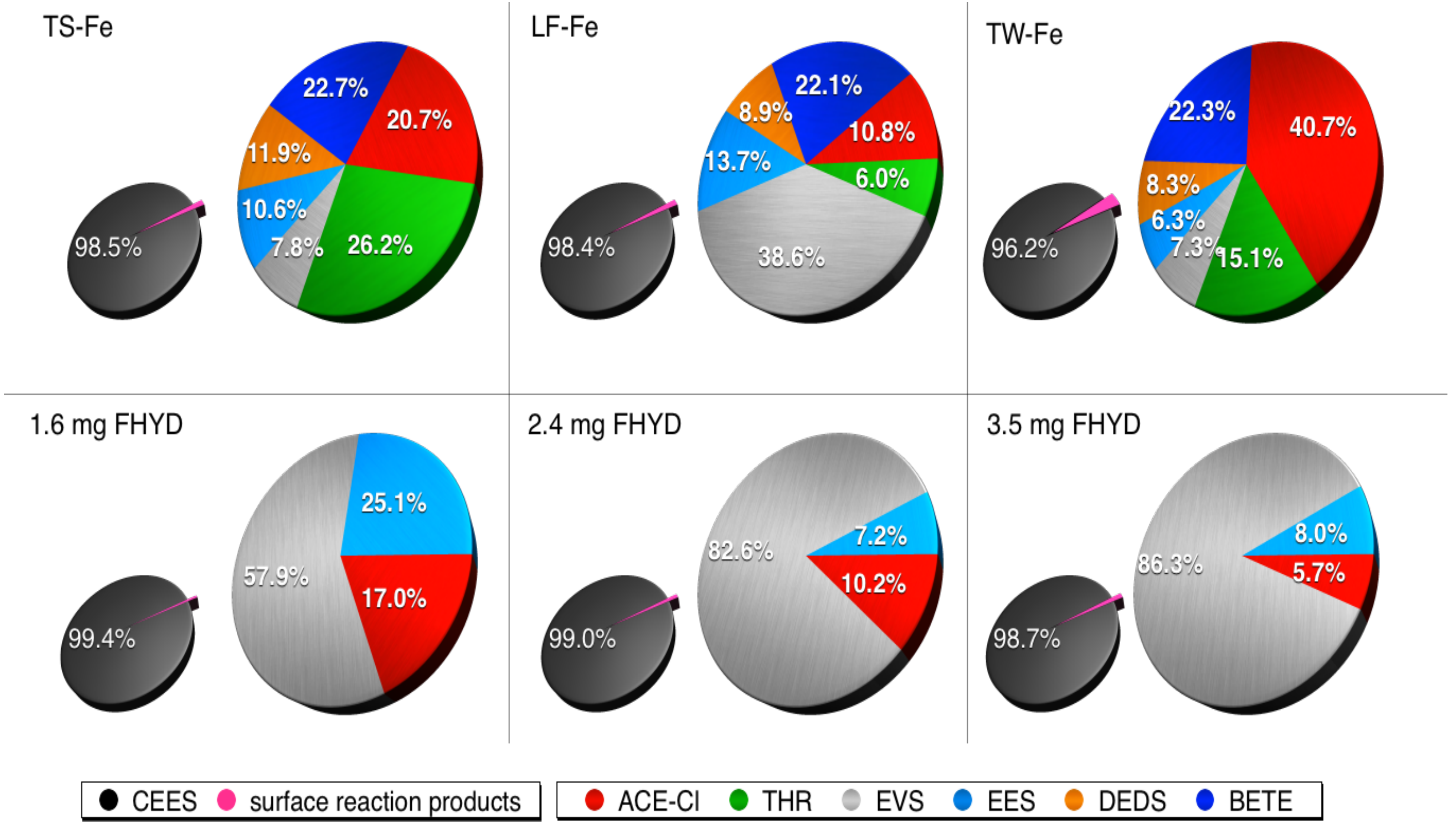
Active Ferrihydrite phase on cotton: CEES



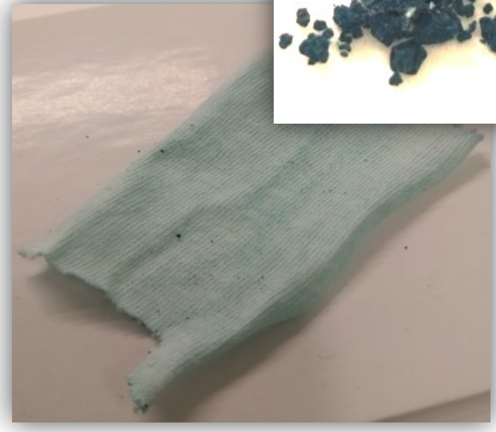


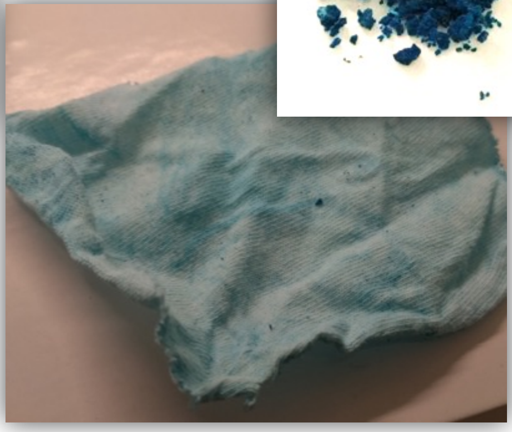


Active Ferrihydrite phase on cotton: extract analysis



Active copper phase on cotton





Swatch from Towel

Copper (hydr)oxide

Copper oxide

<2 % CuO

Swatch from T-shirt

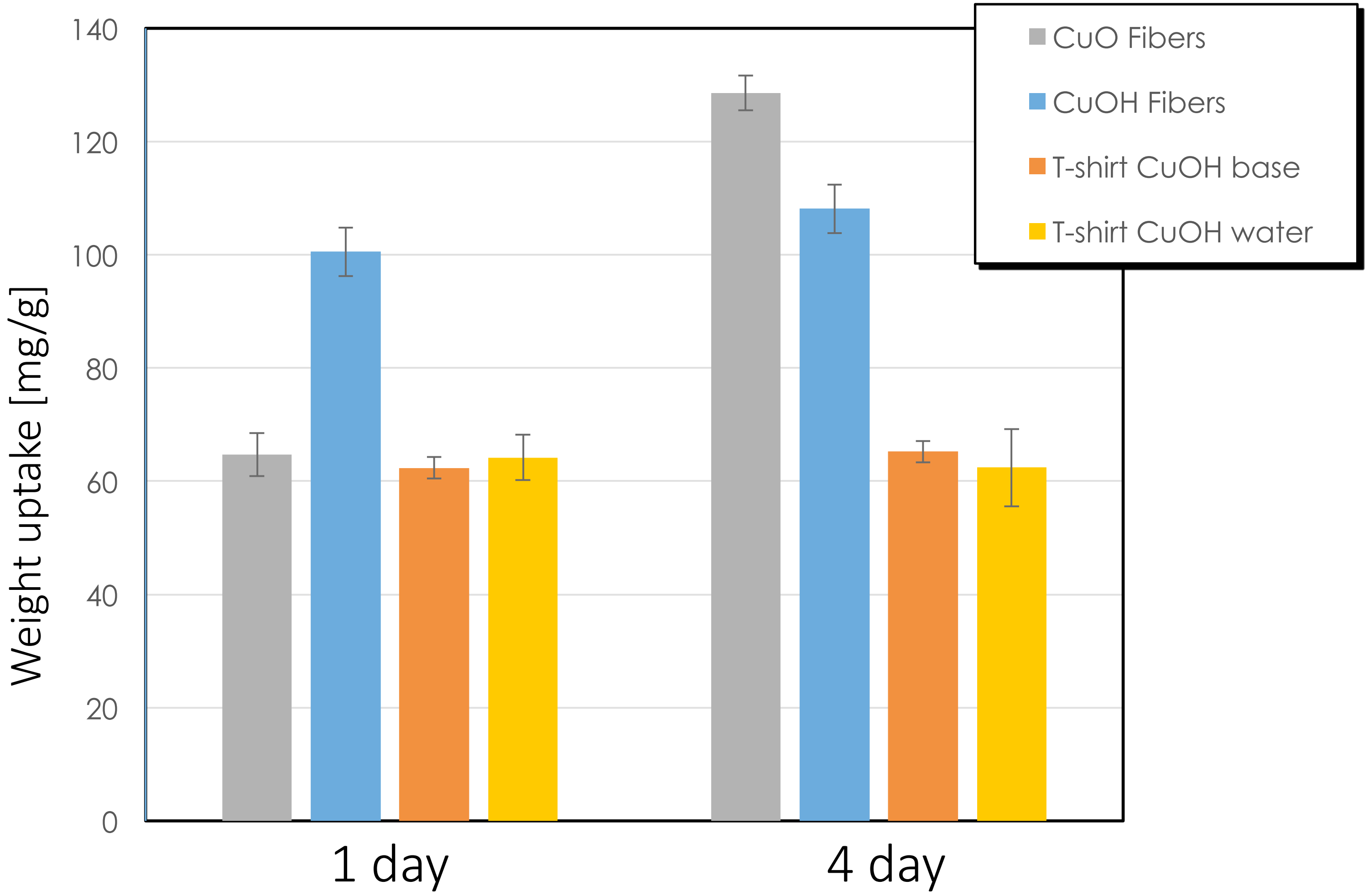
Copper (hydr)oxide

Washed with water

Washed with base

TA in air:
5 % CuO

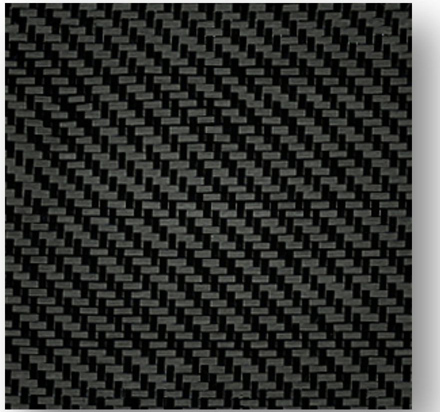
Active copper phase on cotton fibers-DMCP



Copper content< 2 %

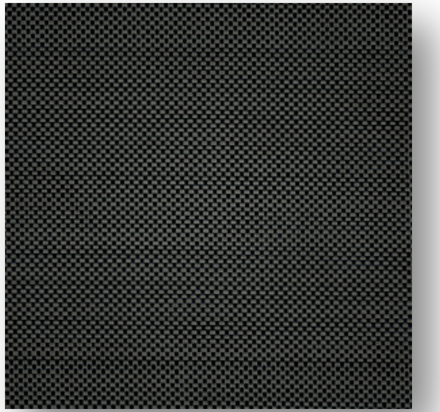
Active copper phase on carbon fibers

Types of Carbon

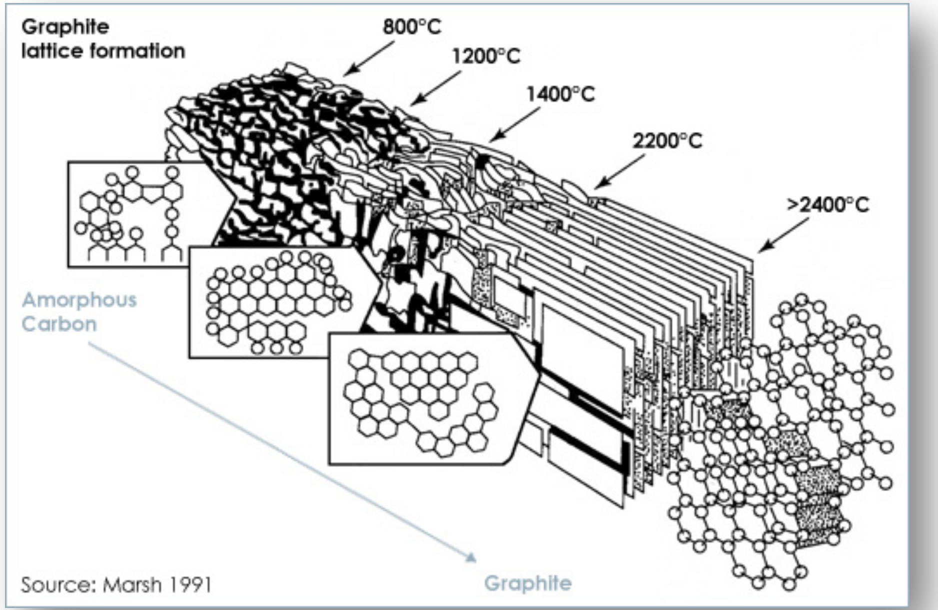


Graphite fiber swatch

Fibers
from swatch



Carbon swatch

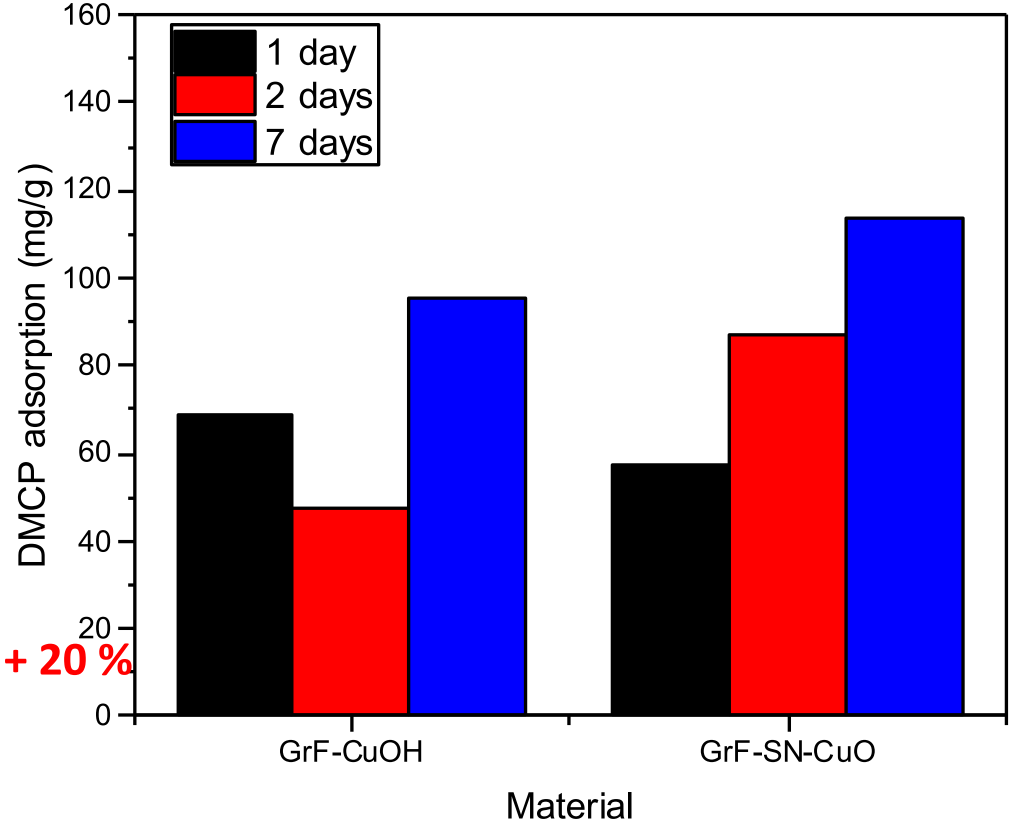


Active copper phase on graphitic carbon fibers

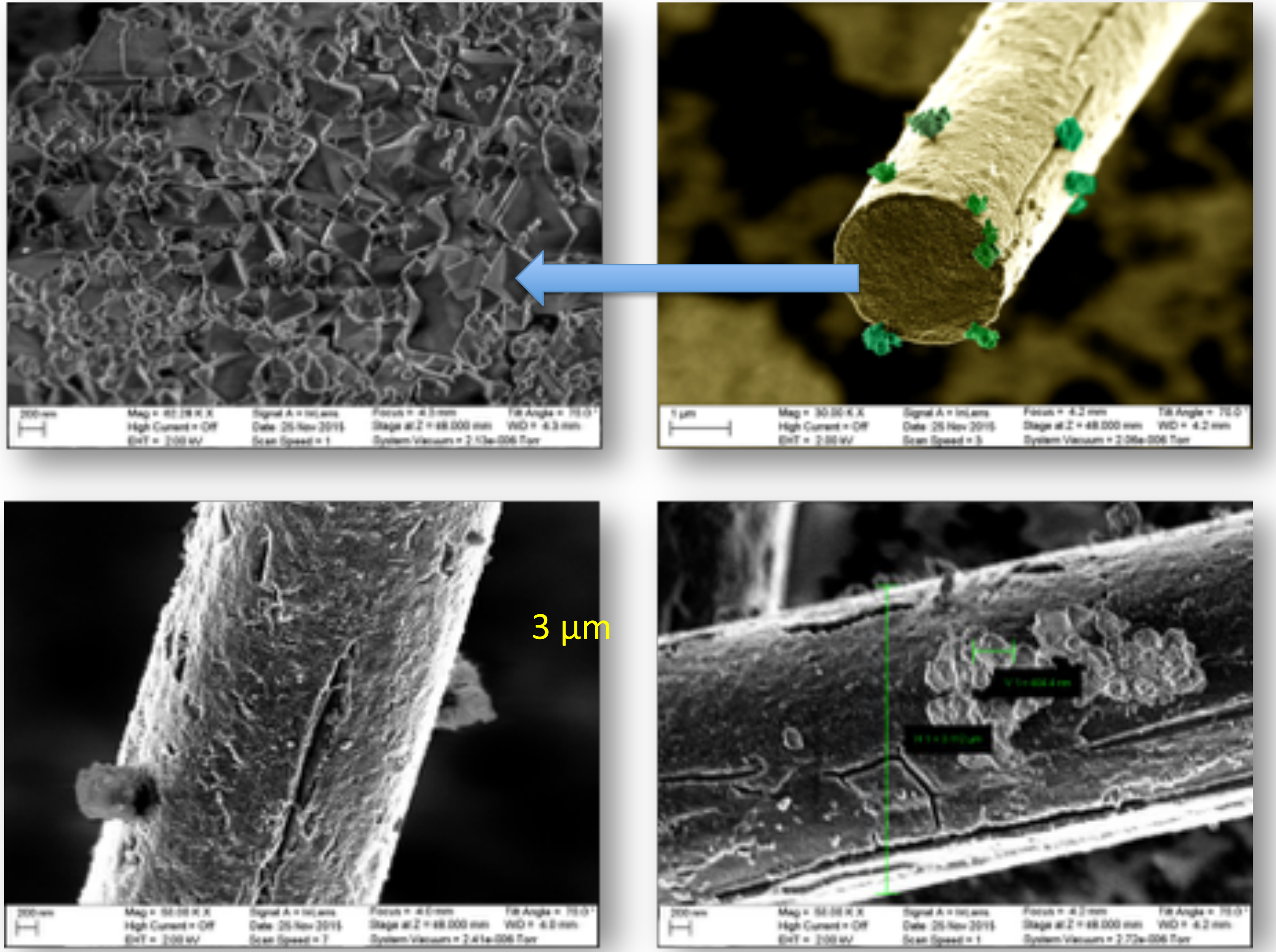
< 3 % CuO

Material	DMCP adsorption mg/g	
	1 day	1 week
GrF+CuOH	69.1	95.2
GrF-NS+CuO	57.1	113.6

+ 20 %

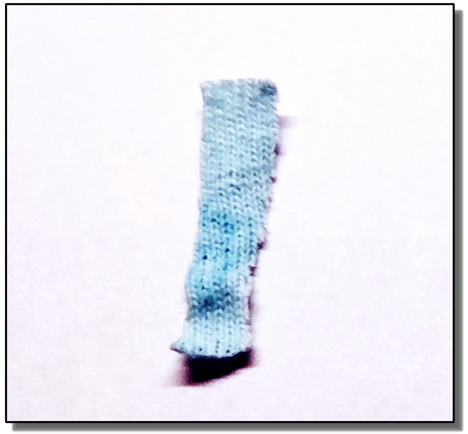


Active copper phase on carbon fibers-Cu-BTC



Sensing capability

Swatch from T-shirt, $Cu(OH)_2$, base washed




initial

24 hours

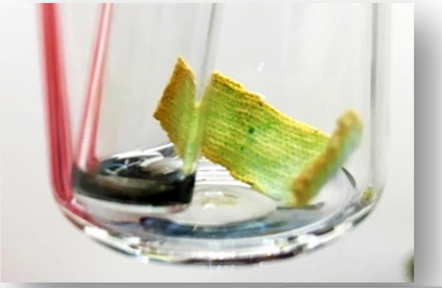
Swatch from Towel, CuO

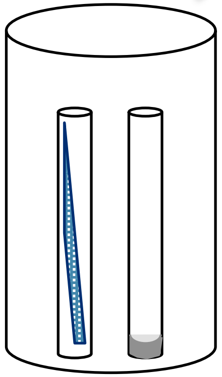

initial

24 hours

DMCP

3 hours

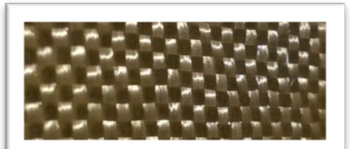




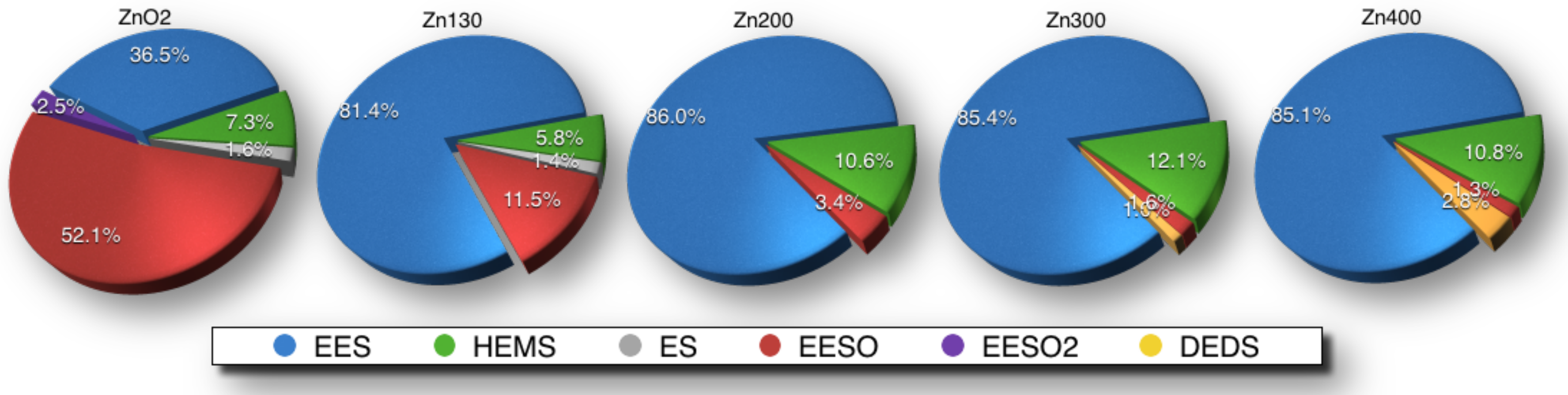
3 hours

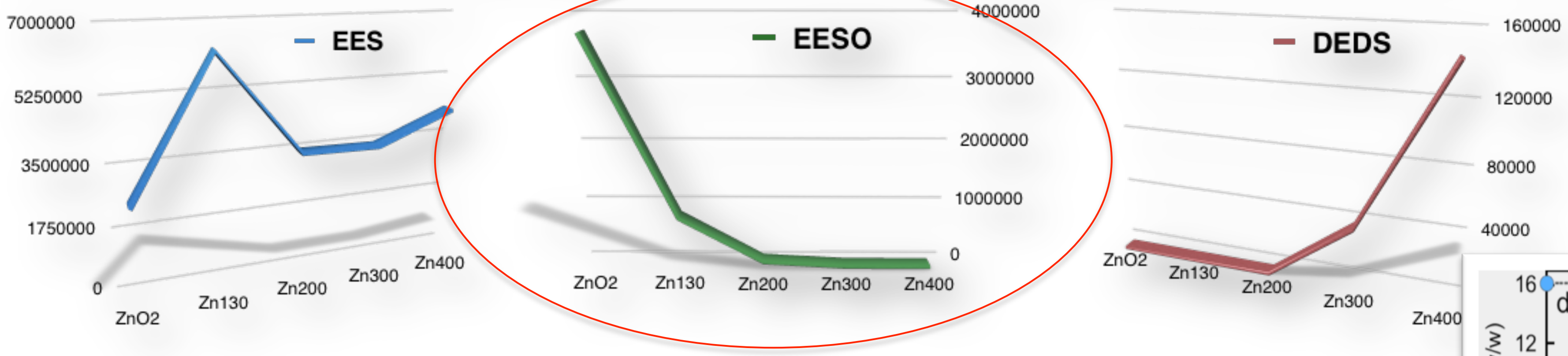
CF-SN+CuON

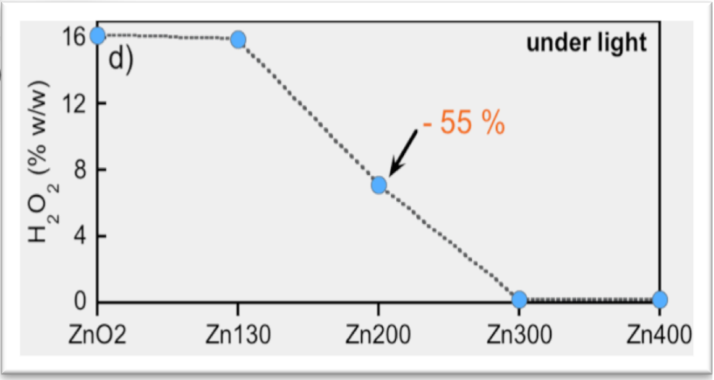

CF-SN+CuO



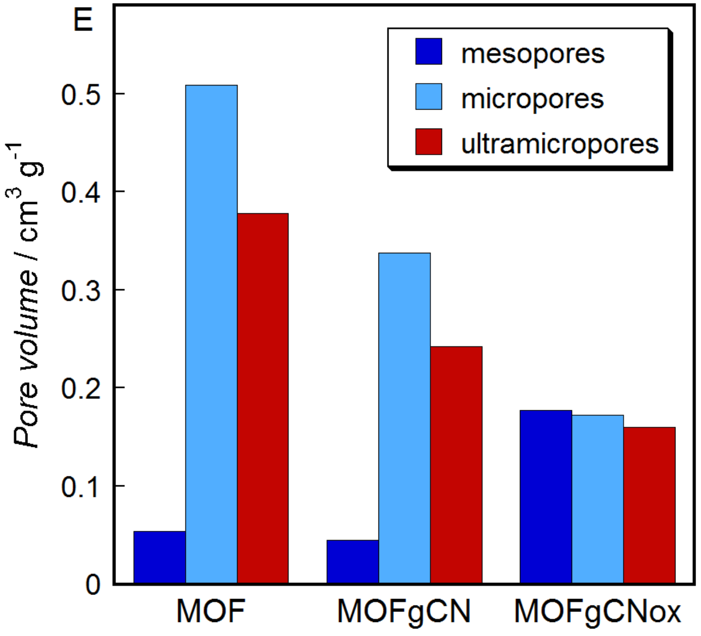

ZnO_2 activity: EES conversion- Extracts analysis

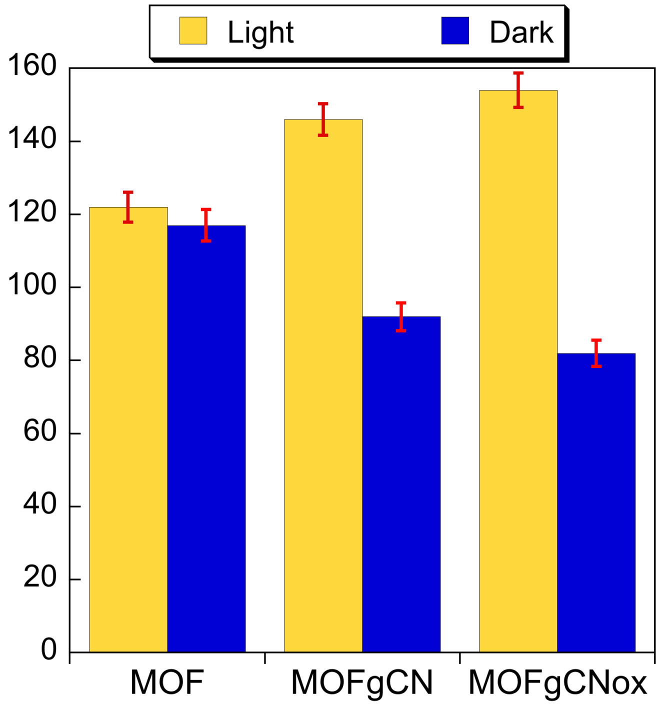


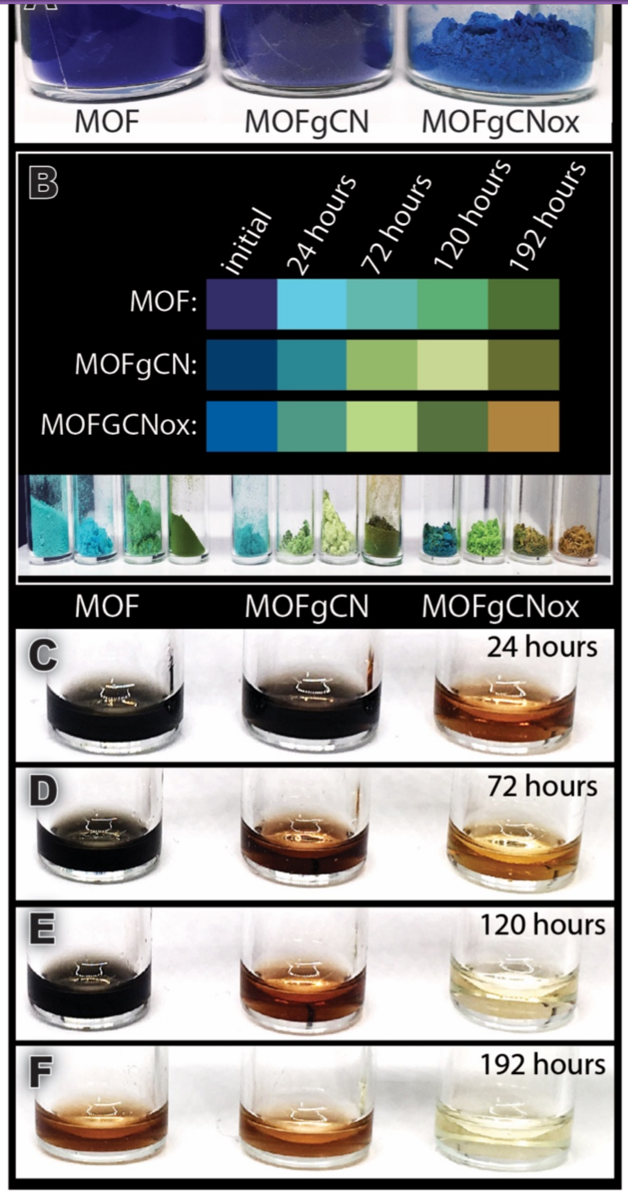




Cu-BTC/g-C_3N_4 composites: Activity- DMCP

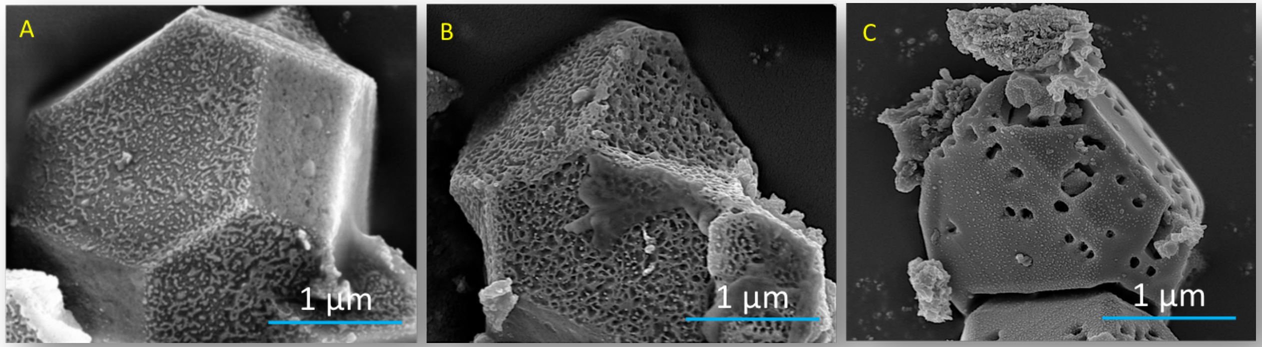


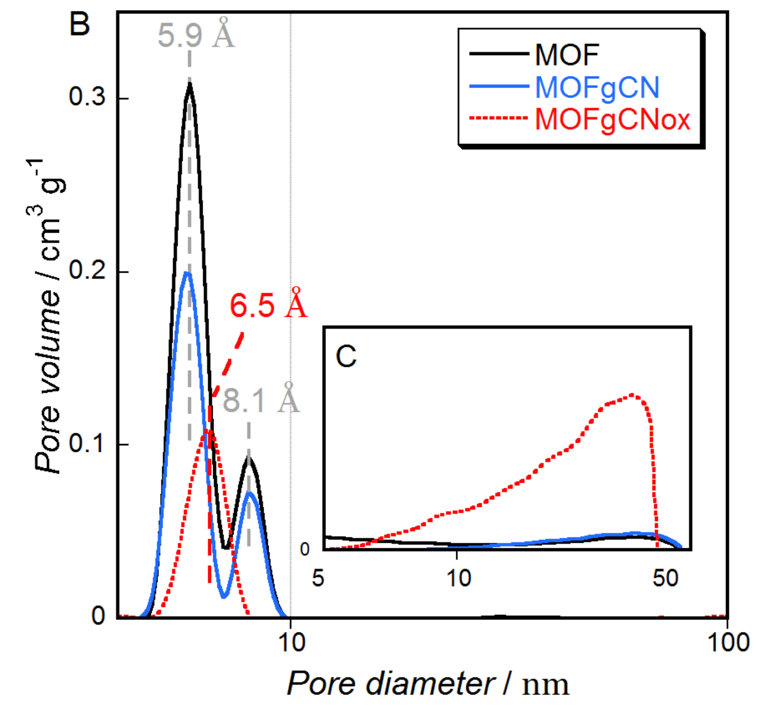


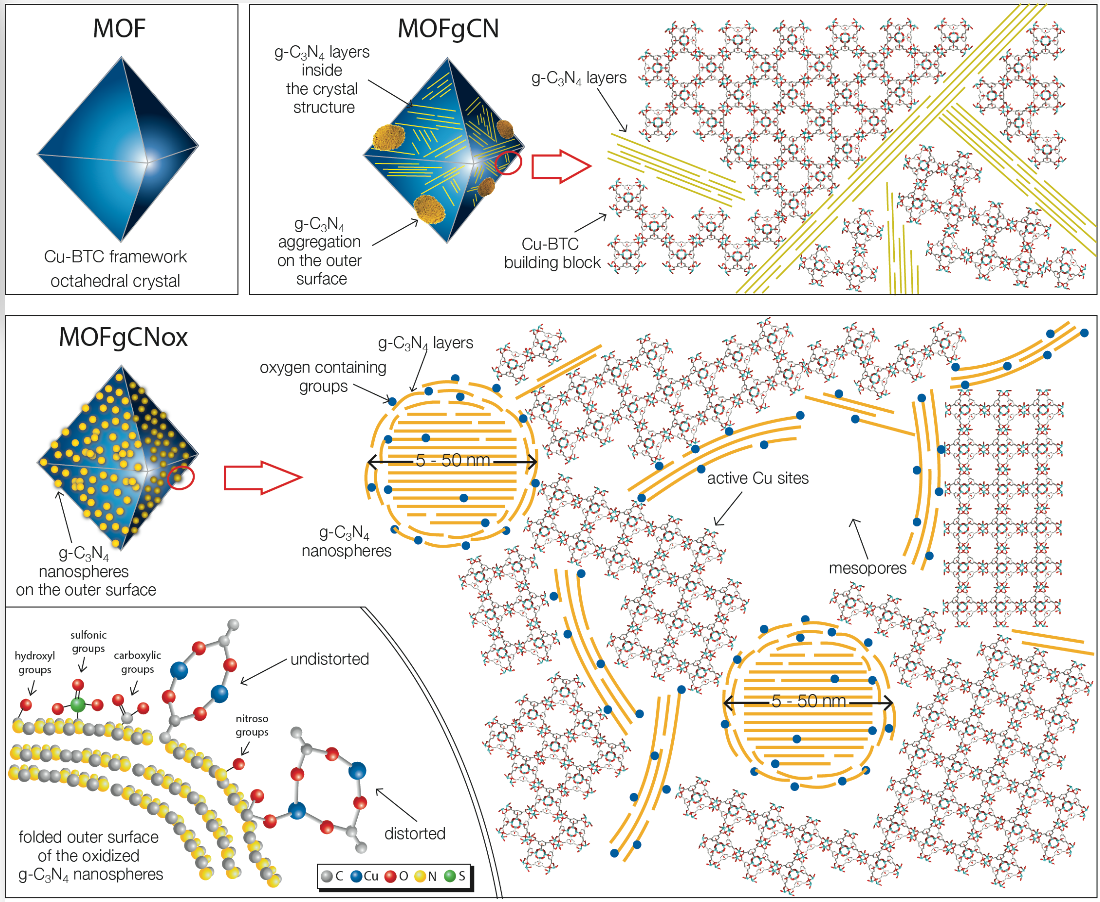


Giannakoudakis, D.A., et al. Small, 2016, in press

Cu-BTC/g-C_3N_4 composites: Porosity

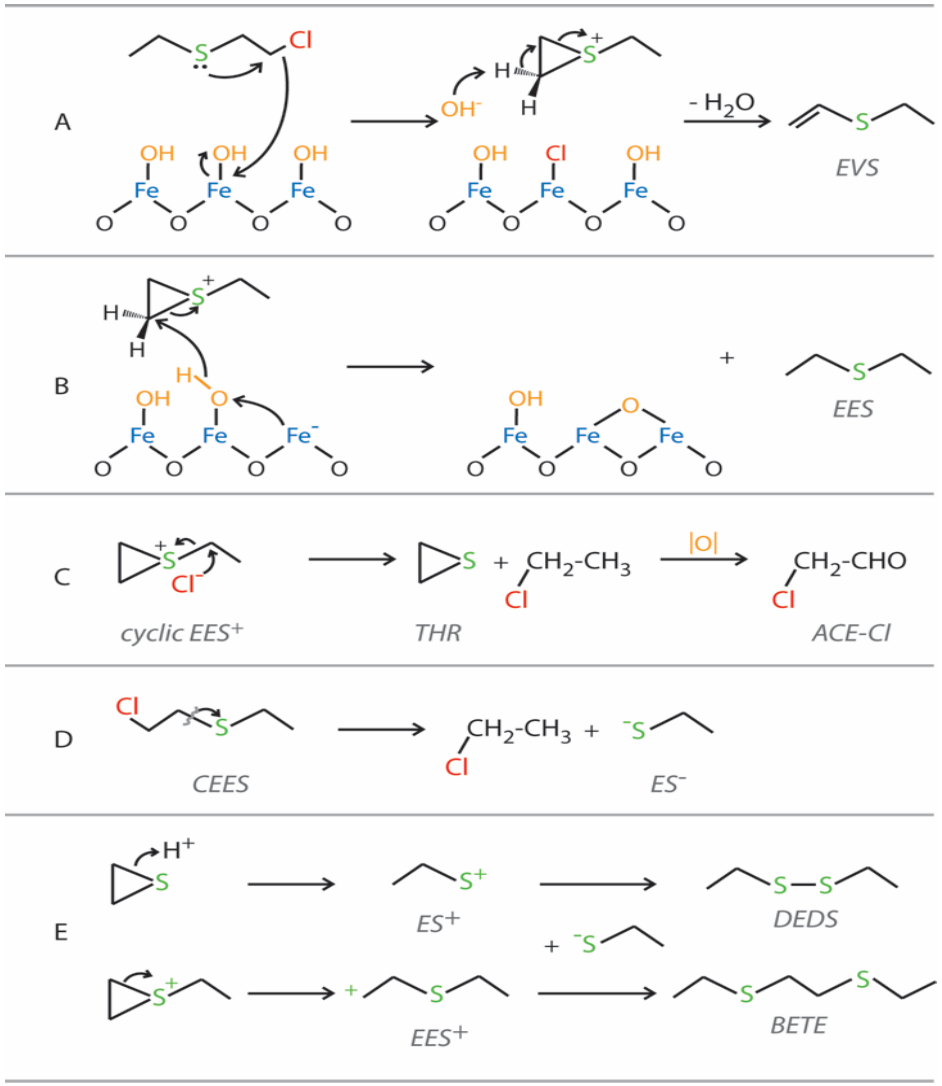


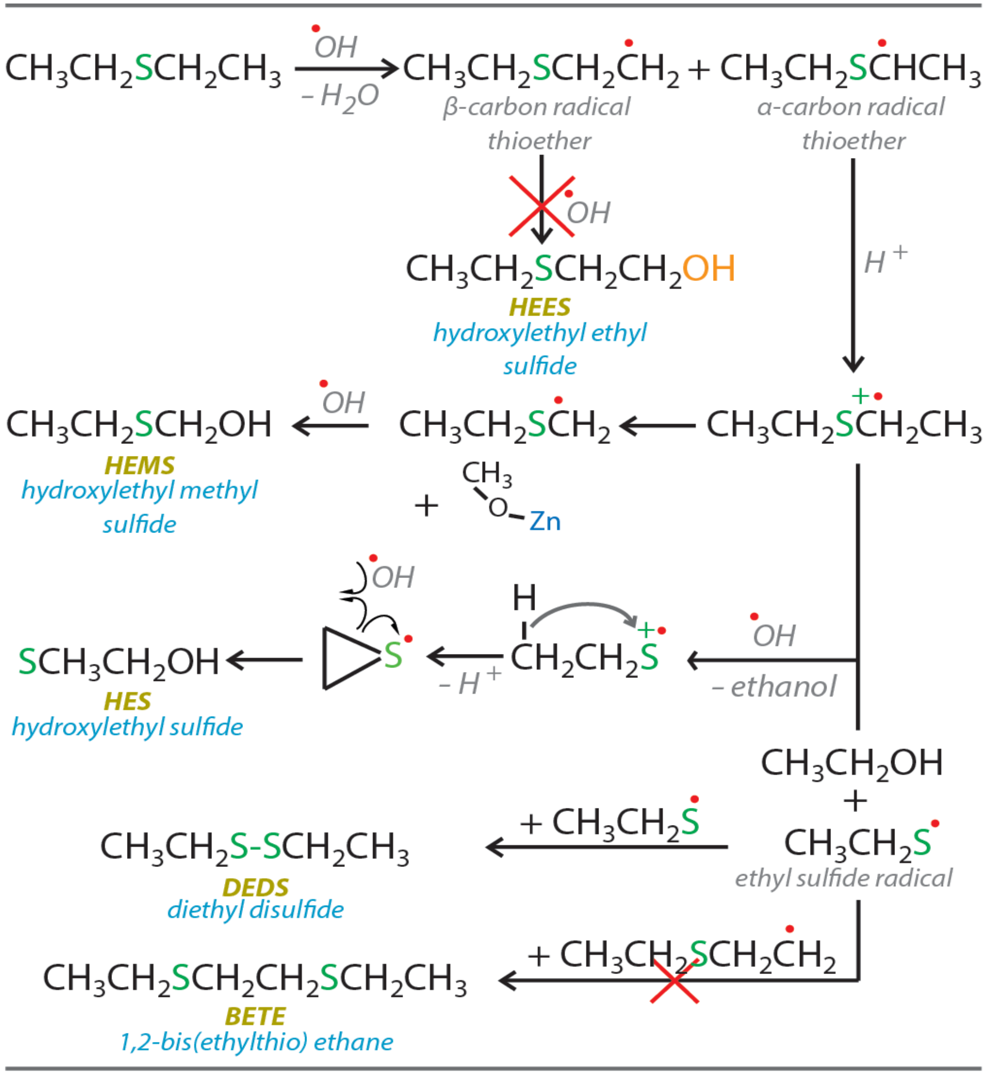




Giannakoudakis, D.A., et al. Small, 2016, in press

General decontamination mechanism



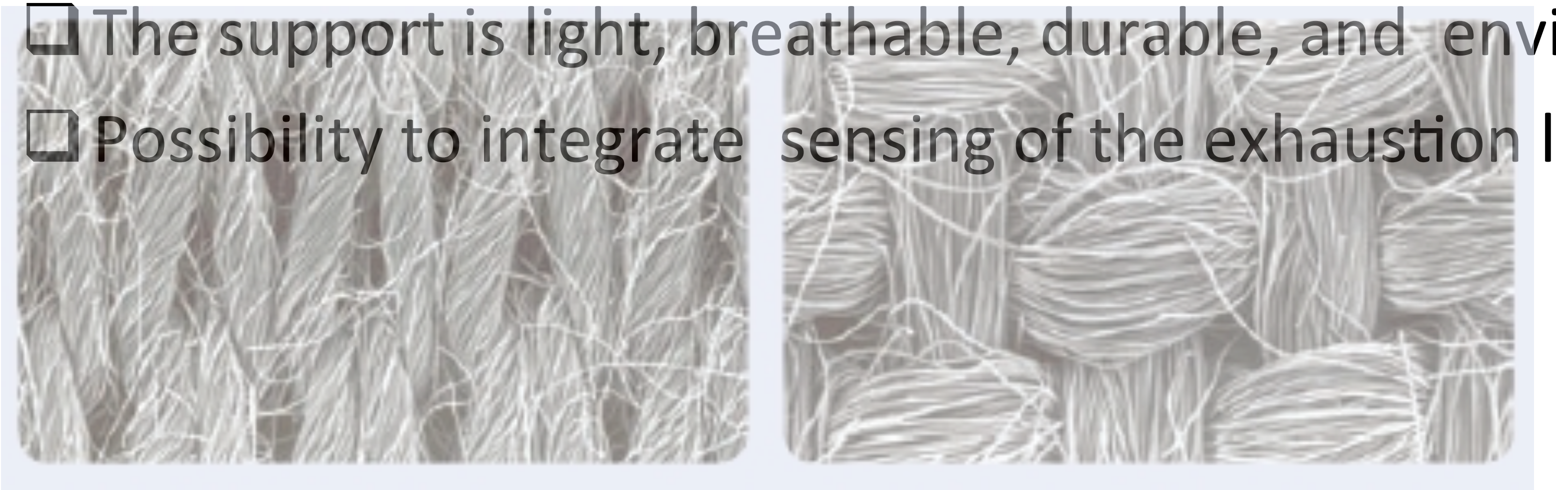


Key Findings

- Defects in the catalytic phase of metal (hydr)oxide promote reactivity towards CWA
- Addition of GO increases the surface heterogeneity and thus activity
- Deposition of active phase on fibers results in synergist effect related to the surface distribution of active phase and defects
- The color change of the active phase/fabrics might be an indicative of the exhaustion level of the protection layers
- **High surface area of carbon cloths/textiles and electrical conductivity make them potential candidates for smart and reactive fabrics**

Why Modified Carbon fibers as a support for an active phase ?

- ❑ Their surface can be chemically modified to create site for active phase strong/covalent attachment.
- ❑ On the interface new chemistry beneficial for the decontamination can be formed
- ❑ The surface reaction products can de adsorbed in the developed pore system enhancing adsorption of organic molecules
- ❑ The conductivity of carbon phase may promote redox/oxidation reactions
- ❑ The support is light, breathable, durable, and environmentally stable
- ❑ Possibility to integrate sensing of the exhaustion level



Acknowledgement

This work was supported by

ARO (Army Research Office) grant W911NF-13-1-0225

Dr. Christopher Karwacki (ECBDC)

CONTRIBUTORS

Javier Arcibar-Orozco

Dimitrios A. Ginnakoudakis

Marc Florent

Rajiv Wallace

TJB